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# EFFECT OF CURE UPON CROSSLINKING, CHAIN SCISSION, AND COMPRESSION SET IN AN IRRADIATED RUBBER VULCANIZATE

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## ADMINISTRATIVE INFORMATION

The work reported is part of a project sponsored by the Bureau of Ships under RDT&E Project Number S-R007 11 01, Task 0556. The project is described in this Laboratory's USNRDL Technical Program for Fiscal Years 1962 and 1963, 1 July 1961, where it is designated Program A-6, Problem 1. Progress in the project is reported most recently in Quarterly Progress Report, 1 October to 31 December 1961, January 1962.

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## ABSTRACT

A compressed natural rubber vulcanizate was exposed to $10^8$ r of gamma radiation and allowed to reach its set length at 40°C after release from compression. Compression set, crosslinking and scission of the elastomer network varied with degree of cure.

$$S = -0.66 \times 10^{-18} C_o + 95.1$$

$$C_r = 0.26 C_o + 21.5 \times 10^{18}$$

$$\Delta C_o = 0.60 C_o + 2.4 \times 10^{18}$$

where S = Percent compression set
$C_o$ = Number of vulcanization crosslinks per gram of specimen (degree of vulcanization)
$C_r$ = Number of crosslinks engendered per gram of specimen in the compressed state by $10^8$ r
$\Delta C_o$ = Number of vulcanization crosslinks scissioned per gram by $10^8$ r.

The average radiation yield (G) for chain scission and for crosslinking in the dose region from 0 to $10^7$ r was 0.75 and 1.3, respectively. 9,10-Phenanthrenequinone and 1,4-naphthoquinone functioned as anti-rads at $10^8$ r and reduced compression set moderately below that predicted from degree of cure.

## SUMMARY

### The Problem

The problem was to determine the relationship between compression set induced by radiation and the degree of vulcanization for rubber specimens, and to determine the ability of various additives to reduce radiation-induced compression set.

### The Findings

Compression set due to a $10^8$ r dose of gamma radiation decreases linearly from 92 to 75 percent as the degree of vulcanization increases from $5 \times 10^{18}$ to $30 \times 10^{18}$ crosslinks per gram of specimen. At $20 \times 10^{18}$ crosslinks per gram, the crosslinking density above which specimens are always tightly cured, compression set is 82 %. 9,10-Phenanthrenequinone and 1,4-naphthoquinone functioned as anti-rads at $10^8$ r and reduced compression set moderately below that predicted from degree of cure.

## INTRODUCTION

This report deals with the effect of additives and cure on compression set, crosslinking, and chain scission in an irradiated rubber vulcanizate. It is part of a continuing investigation on the interaction of nuclear radiation with elastomeric materials.[1-4] These elastomers are of interest for their possible use as component parts of devices which may be used in prolonged or intense nuclear radiation fields on earth or in space.

It was shown previously by the authors that there was a linear relationship between radiation-induced compression set and degree of cure of a rubber cylinder:[1]

$$S = kC_o + K \tag{1}$$

where S = Percent compression set
$C_o$ = Number of pre-irradiation crosslinks per gram
k and K = Constants for a particular energy absorbed per gram.

The earlier study was based on different degrees of cure which were the result of the additive, whereas the present study used samples of identical composition which were cured for different lengths of time. One purpose of the present study was to confirm the relationship expressed in Eq. 1.

Evaluation of an anti-rad can be made by comparing the expected value of compression set, based on the measurement of pre-irradiation crosslinks, to the experimental value. If the experimental value is significantly less than that predicted, the added compound can be considered an anti-rad. If greater, radiation sensitization can be assumed.

The present study also endeavored to evaluate as anti-rads the following types of compounds; aromatic hydrocarbons, hydrazines, phenols, quinoids, organo-metallics, mercaptans, and amines.

Previous work established a method for determining radiation yields of chain scission and crosslinking for rubber vulcanizates. This method combined set and solvent-swelling measurements, and was applied to the vulcanizates described herein.

## EXPERIMENTAL

Test specimens were measured for length, and were compressed, irradiated in a nitrogen atmosphere, released, allowed to recover at 40°C, re-measured for compression set, and then measured for crosslinking by solvent swelling. Also, initial crosslinking (cure) was determined using similar specimens. Statistical treatment of the compression set versus initial crosslinking data established Eq. 1 as the regression line relating set and cure at a $10^8$ r dose.[5]

### Rubbers

All rubber specimens were cylinders cured in a mold. The dimensions of the mold forms were 0.5-in. depth and 0.425-in. diameter.

Fourteen rubber stocks of identical composition but having different states of cure were prepared by varying the cure time. The following weight recipe and a 260°F cure were used; deproteinized pale crepe, 100; sulfur, 2; zinc oxide, 3; zinc dibutylidithiocarbamate, 0.25; 2-mercaptobenzothiazole, 0.4; and carbon (Thermax), 50. Table 1 shows the cure times used and the extent of crosslinking they produced.

Also, fifty-six rubber stocks of the above composition were prepared except that each contained 5 parts of a unique additive to be evaluated as an anti-rad. Cure conditions were 20 minutes at 260°F, but the chemical nature of the additive affected the degree of cure so that a variety of cures were obtained. Test specimens were similar in recipe, shape, and preparation to the additive rubbers evaluated for radiation resistance in the previous study.[1] The additives tested are listed in Table 2 along with 47 additives previously evaluated for anti-rad behavior[1] but re-evaluated herein because of a difference in method of calculating compression set. The latter are identified by the footnote symbol b.

TABLE 1

Pre-Irradiation Crosslinks and Compression Sets for Rubber Stocks Without Additives, Cured for Different Times at 260°F

| Stock | Cure Time (min) | Number of Pre-Irradiation Crosslinks per gram, $C_o$[a] ($\times 10^{-18}$) | Blank Factor F[b] | Compression Set[a] |
|---|---|---|---|---|
| 1 | 6.5 | 7.8 | 0.917 | 90.3 |
| 2 | 7 | 8.1 | 0.933 | 90.55 |
| 3 | 7.5 | 8.5 | 0.933 | 90.8 |
| 4 | 8 | 9.5 | 0.945 | 90.2 |
| 5 | 8.5 | 10.3 | 0.945 | 87.0 |
| 6 | 9 | 10.7 | 0.959 | 85.2 |
| 7 | 9.5 | 14.8 | 0.968 | 81.7 |
| 8 | 10 | 20.3 | 0.987 | 82.4 |
| 9 | 15 | 23.0 | 0.991 | 81.6 |
| 10 | 20 | 23.5 | 0.995 | 81.7 |
| 11 | 20 | 19.3 | 0.996 | 80.5 |
| 12 | 25 | 23.2 | 0.996 | 81.0 |
| 13 | 30 | 22.7 | 0.996 | 77.7 |
| 14 | 35 | 22.6 | 0.996 | 77.5 |

a. Crosslinking and compression set values are averages from quintuplicate experiments.

b. Blank factors are averages from triplicate experiments.

Compression and Irradiation

Specimens were measured and compressed to 0.375 in. in compression jigs, as previously described.[1] This was done in a nitrogen-filled glove box so that the specimens were sealed within their spacers in a nitrogen atmosphere. Irradiations to $10^7$ or $10^8$ r were performed with a cobalt-60 source which provided $10^8$ r in 530 hrs. Dosimetry was done with the Fricke ferrous sulfate dosimeter.[5] After irradiation, specimens were released from compression and allowed to recover for 3 weeks at 40°C before set length was measured. Control specimens of each stock were treated exactly as test specimens, except that they were not irradiated. The set lengths of the controls were used to calculate blank factors, F (see section headed "Compression Set"), which were used in the calculation of compression sets of test specimens.

Compression set and crosslinking data determined for vulcanizates in the previous study were re-evaluated. These vulcanizates were irradiated with gamma radiation from reactor spent fuel elements.

Crosslinking and Radiation Yields

The number of crosslinks per gram of specimens (crosslinking density) was determined by the solvent-swelling procedure of the previous experiment.[1] Pre-irradiation and post-irradiation crosslinking densities are denoted by $C_o$ and C, respectively. Also determined by those procedures were the number of vulcanization crosslinks per gram of specimen remaining after irradiation, $C_v$; the number of vulcanization crosslinks scissioned per gram of specimen due to irradiation, $\Delta C_o$; the number of crosslinks engendered per gram of specimen in the compressed state by irradiation, $C_r$; and radiation yields of chain scission and crosslinking for the dose region from 0 to $10^7$ r. The method for determining radiation yields combines set and solvent-swelling measurements.

Compression Set

Compression set for a test specimen is defined by Eq. 2.

$$\text{Compression set } (\%) = \frac{(\ell_o F - \ell_s)\,100}{\ell_o F - \ell_c} \qquad (2)$$

where $\ell_o$ = Test specimen length before compression.
$\ell_s$ = Test specimen length after irradiation, release from compression, and recovery.
$\ell_c$ = Test specimen when compressed.
F = Control, or blank factor.

TABLE 2

Compression Sets for Additive Rubbers

| Vulcanizate (Designated by Additive) | Footnotes | (Blank Factor) F | Experimental Compression Set | Predicted Compression Set[e] | Difference Between Predicted and Experimental | Difference Required for Statistical Significance at 95% Level |
|---|---|---|---|---|---|---|
| 9,10-Phenanthrenequinone | a | 0.996 | 58 | 75 | 17 | 7 |
| 1,4-Naphthoquinone | a | 0.997 | 59 | 79 | 20 | 7 |
| N-(2-Aminoethyl)-N-ethyl-m-toluidine | a,b | 0.976 | 66 | 75 | 9 | 12 |
| 1,3-Diphenyltriazine | a,b | 0.974 | 67 | 78 | 11 | 12 |
| N,N-Dimethyl-p-phenylenediamine | a,b | 0.974 | 69 | 77 | 8 | 12 |
| 2,2'-Bipyridine | a,d | 0.989 | 69 | 76 | 7 | 7 |
| 2-Amino-4-methylpyridine | a,d | 0.990 | 70 | 76 | 6 | 7 |
| 8-Aminoquinoline | a,b | 0.978 | 71 | 78 | 7 | 12 |
| N,N'-Diphenyl-p-phenylenediamine | a,b | 0.960 | 71 | 79 | 8 | 12 |
| Triphenylstilbine | a | 0.984 | 72 | 78 | 6 | 7 |
| 1-Methylheptylamine | a,b | 0.964 | 72 | 75 | 3 | 12 |
| N-1-Naphthylethylenediamine | a,b | 0.968 | 73 | 76 | 3 | 12 |
| N,N-Dimethyl-p-1-naphthylazoaniline | a,b | 0.968 | 73 | 79 | 6 | 12 |
| 2,4-Dinitrophenylhydrazine | a | 0.995 | 73 | 79 | 6 | 7 |
| N-Methyldiphenylamine | a,b | 0.970 | 73 | 80 | 7 | 7 |
| Tribenzylamine | a,b | 0.978 | 73 | 80 | 7 | 12 |
| Quinoline | a,b | 0.978 | 73 | 79 | 6 | 12 |
| 2,2'-Biquinoline | a,b | 0.974 | 73 | 80 | 7 | 12 |
| N,N,N',N'-Tetramethyl-p-phenylenediamine | a,b | 0.974 | 73 | 80 | 7 | 12 |
| o-Aminophenol | a | 0.997 | 74 | 78 | 4 | 7 |
| p-sec-Amylaniline | a,b | 0.976 | 74 | 79 | 5 | 12 |
| Di-iso-amylamine | a,b | 0.970 | 74 | 79 | 5 | 12 |
| Biphenyl | a | 0.995 | 74 | 79 | 5 | 7 |
| N-Methylaniline | a,b | 0.974 | 74 | 81 | 7 | 12 |
| Pyrene | a | 0.995 | 74 | 80 | 6 | 7 |
| 1-Naphthylamine | a,b | 0.976 | 74 | 80 | 6 | 12 |
| Phenyl Sulfide | a | 0.995 | 74 | 79 | 5 | 7 |
| Fluoranthrene | a | 0.996 | 74 | 80 | 6 | 7 |
| N,N-Dimethyldodecylamine | a,b | 0.970 | 75 | 78 | 3 | 12 |
| Hydroquinone | a | 0.994 | 75 | 78 | 3 | 7 |
| Diphenylamine | a,b | 0.978 | 75 | 79 | 4 | 12 |
| 3,5-Dimethylpyrazole | a,b | 0.970 | 75 | 78 | 3 | 12 |
| Acridine | a,d | 0.989 | 75 | 82 | 7 | 7 |
| 2-Vinylpyridine | a,b | 0.972 | 75 | 80 | 5 | 12 |
| o-Phenylenediamine | a,b | 0.982 | 75 | 76 | 1 | 12 |
| 1,2-Naphthoquinone | a | 0.974 | 75 | 83 | 8 | 7 |
| N,N-Di-n-propylaniline | a,b | 0.976 | 75 | 80 | 5 | 12 |
| Triphenyl Bismuthine | a | 0.993 | 76 | 79 | 3 | 7 |
| 2,2-Diphenyl-1-picrylhydrazyl | a | 0.996 | 76 | 79 | 3 | 7 |
| 2,4-Diamino-6-phenyl-s-triazine | a,b | 0.974 | 76 | 80 | 4 | 12 |
| Butyl Disulfide | a | 0.992 | 76 | 81 | 5 | 7 |
| Phenanthrene | a | 0.995 | 77 | 80 | 3 | 7 |
| N-Cyclohexyl-N'-phenyl-p-phenylenediamine | d | 0.986 | 77 | 81 | 4 | 7 |

(Continued)

TABLE 2 (Contd)

Compression Sets for Additive Rubbers

| Vulcanizate (Designated by Additive) | Footnotes | (Blank Factor) F | Experimental Compression Set | Predicted Compression Set[a] | Difference Between Predicted and Experimental | Difference Required for Stastical Significance at 99% Level |
|---|---|---|---|---|---|---|
| 1,3-Di-o-tolylguanidine | a,d | 0.947 | 77 | 85 | 8 | 7 |
| N-Phenyl-N'-isopropyl-p-phenylenediamine | | 0.994 | 77 | 81 | 4 | 7 |
| N,N'-Diphenylbenzidine | a,b | 0.974 | 77 | 80 | 3 | 12 |
| Triphenylamine | a,b | 0.976 | 77 | 79 | 2 | 12 |
| p-Quaterphenyl | a | 0.993 | 77 | 80 | 3 | 7 |
| N-iso-Amylaniline | a,b | 0.986 | 77 | 80 | 3 | 12 |
| m-Terphenyl | a | 0.997 | 77 | 80 | 3 | 7 |
| N,N,N',N'-Tetramethylbenzidine | a,b | 0.962 | 77 | 81 | 4 | 12 |
| Carbazole | a,b | 0.972 | 78 | 80 | 2 | 12 |
| Phenyl Disulfide | a | 0.992 | 78 | 84 | 6 | 7 |
| p-Terphenyl | a | 0.996 | 78 | 80 | 2 | 7 |
| N,N'-Diphenylethylenediamine | a,b | 0.974 | 78 | 80 | 2 | 12 |
| Triphenylmethane | a | 0.996 | 78 | 79 | 1 | 7 |
| iso-Butyl Sulfide | a | 0.991 | 78 | 81 | 3 | 7 |
| p-Aminophenol | a | 0.997 | 78 | 79 | 1 | 7 |
| p-Phenylenediamine | a,b | 0.976 | 78 | 77 | -1 | 12 |
| Chrysene | a | 0.992 | 78 | 80 | 2 | 7 |
| Diphenylmercury | a | 0.985 | 78 | 74 | -4 | 7 |
| Cystine | a | 0.997 | 78 | 78 | 0 | 7 |
| Naphthalene | a | 0.995 | 78 | 80 | 2 | 7 |
| Phenol | a | 0.991 | 79 | 80 | 1 | 7 |
| Hexamethylenetetramine | a,b | 0.984 | 79 | 77 | -2 | 12 |
| iso-Butyl Disulfide | a | 0.995 | 79 | 80 | 1 | 7 |
| 2-Benzylpyridine | a,b | 0.966 | 79 | 80 | 1 | 12 |
| Dicyclohexylamine | a,d | 0.950 | 79 | 82 | 3 | 7 |
| 4,4'-Oxydiphenol | a | 0.995 | 79 | 78 | -1 | 7 |
| Dibutyltin Dichloride | a | 0.986 | 79 | 82 | 3 | 7 |
| N,N-Dimethylaniline | a,b | 0.972 | 79 | 80 | 1 | 12 |
| o-Terphenyl | a | 0.995 | 79 | 80 | 1 | 7 |
| 2-n-Amylpyridine | a,b | 0.974 | 80 | 80 | 0 | 12 |
| Tri-iso-amylamine | a,b | 0.974 | 80 | 80 | 0 | 12 |
| Anthraquinone | a | 0.995 | 80 | 79 | -1 | 7 |
| Resorcinol | a | 0.994 | 80 | 79 | -1 | 7 |
| Aniline | a,b | 0.984 | 80 | 80 | 0 | 12 |
| Butyl Sulfide | a | 0.995 | 80 | 79 | -1 | 7 |
| p,p'-Biphenol | a | 0.995 | 80 | 78 | -2 | 7 |
| Carbanthrene Khaki 2G | c,b | 0.994 | 81 | 82 | 1 | 12 |
| Tetrabutyl Tin | a | 0.993 | 81 | 78 | -3 | 7 |
| N,N'-Dicarbethoxyhydrazine | a | 0.993 | 81 | 81 | 0 | 7 |
| Tetraphenyl Tin | a | 0.993 | 81 | 79 | -2 | 7 |
| Indocarbon CL | c,b | 0.996 | 81 | 80 | -1 | 12 |
| Anthracene | a | 0.996 | 82 | 80 | -2 | 7 |
| N,N'-Dimethyl-p-phenylenediamine | a,b | 0.980 | 82 | 79 | -3 | 12 |
| Benzidine | a,b | 0.972 | 82 | 79 | -3 | 12 |

(Continued)

TABLE 2 (Contd)

Compression Sets for Additive Rubbers

| Vulcanizate (Designated by Additive) | Footnotes | (Blank Factor) F | Experimental Compression Set | Predicted Compression Set[e] | Difference Between Predicted and Experimental | Difference Required for Statistical Significance at 95% Level |
|---|---|---|---|---|---|---|
| Tetraethyl Orthotitanate | a | 0.971 | 82 | 85 | 3 | 7 |
| Dibutyltin Diacetate | a | 0.981 | 82 | 80 | -2 | 7 |
| Hydrazine Sulfate | a | 0.987 | 83 | 79 | -4 | 7 |
| Triphenyltin Chloride | a | 0.981 | 84 | 80 | -4 | 7 |
| Tetraethyl Orthosilicate | a | 0.988 | 85 | 81 | -4 | 7 |
| 1,2,3-Triketohydrindene | a | 0.973 | 85 | 84 | -1 | 7 |
| Copper Phthalocyanine | c,b | 0.990 | 85 | 83 | -2 | 12 |
| 2-Aminobenzimidazole | a,d | 0.962 | 86 | 91 | 5 | 7 |
| Phthalocyanine | c,b | 0.982 | 87 | 84 | -3 | 12 |
| m-Aminophenol | a | 0.992 | 87 | 85 | -2 | 7 |
| Didodecyl Selenide | b | 0.974 | 88 | 83 | -5 | 12 |
| Phloroglucinol | a | 0.982 | 88 | 84 | -4 | 7 |
| Graphite | b | 0.980 | 90 | 83 | -7 | 12 |
| 1,4-Benzoquinone | a | 0.967 | 96 | 91 | -5 | 7 |

a. The chemical formula is given in Eastman Organic Chemicals List No. 42, Distillation Products Industries, Rochester 3, N. Y.

b. Compression set was calculated from previously obtained data[1] and the formula of the present report. Specimens were irradiated with gamma radiation from spent fuel elements of the General Electric Test Reactor at Vallecitos, California.

c. The chemical formula is given in reference 3.

d. Compression set data obtained previously[1] for vulcanizates containing this additive were not used. Instead, new test specimens were prepared. The compression set value given is the average of a quintuplicate experiment.

e. Equation 3 was used to calculate the predicted compression set.

The blank factor, F, is defined by Eq. 3

$$F = \frac{1}{n} \sum_{1}^{n} \frac{\ell_{sc}}{\ell_{oc}} \tag{3}$$

where $\ell_{sc}$ = Set length for a non-irradiated control specimen.
$\ell_{oc}$ = Original length for a non-irradiated control specimen.
n = Number of control specimens.

When the blank factor, F, approaches unity, Eq. 2 becomes the simplified one used in the previous study.[1] The vulcanizates evaluated for compression set in the previous study have been re-evaluated herein. Their compression sets have been recalculated by using the data of the previous study in conjunction with Eq. 3.

## RESULTS AND CONCLUSIONS

Perhaps the most significant contributions of this and the previous study are the quantitative relationships between radiation-induced compression set and cure. The fact that both state of cure and presence of rubber additives affect compression set makes anti-rad evaluation more complex than was previously supposed and subject to a wider degree of experimental error.

### Cure Study

The relationship between compression set induced by a $10^8$ r dose and degree of initial crosslinking (vulcanization) has been determined by two procedures. In Procedure I, rubber stocks were used having different degrees of crosslinking brought about by different cure times. In Procedure II, stocks were used having different degrees of crosslinking brought about by incorporating an additive.

Figure 1 shows the relationship resulting from Procedure I. The curve is the regression line of the compression set and crosslinking data of Table 1 and is defined by Eq. 4:

$$S = -0.66 \times 10^{-18} C_o + 95.1 \tag{4}$$

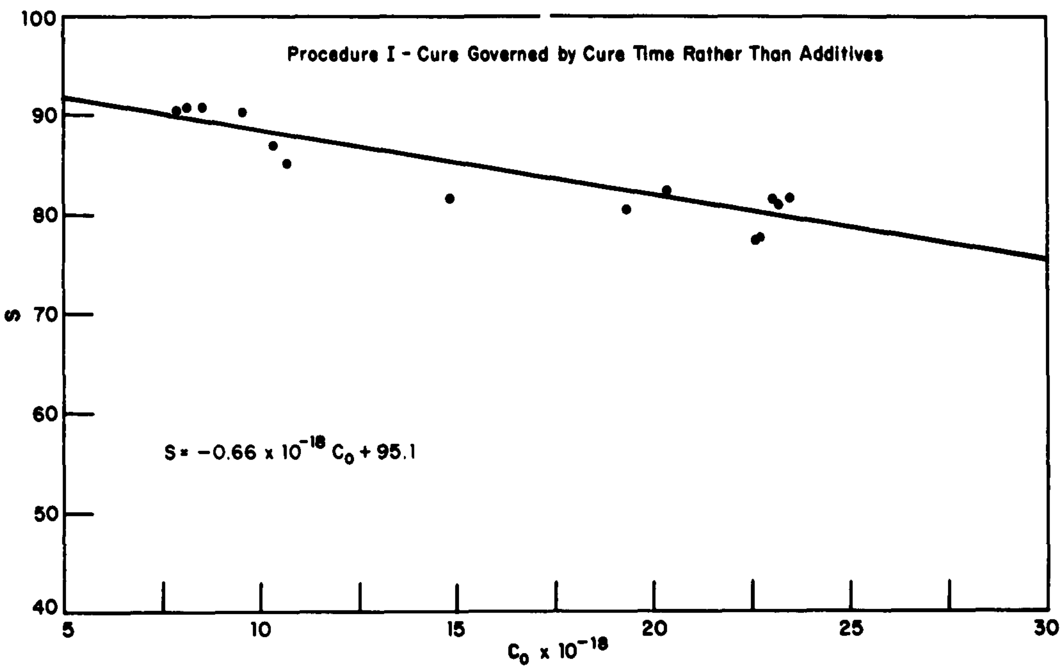


Fig. 1 Compression Set at $10^8$ r Versus Pre-Irradiation Crosslinks - Procedure I.

where $S$ = Percent compression set.
$C_o$ = Number of pre-irradiation crosslinks per gram of cylindrical specimen.

Each data point represents the average from quintuplicate compression sets and quintuplicate solvent-swollen specimens. The blank factor, F (Eq. 3), was determined with triplicates. The standard error in estimating S from $C_o$ by Eq. 5 is 2.1.[5]

Figure 2 shows the relationship resulting from Procedure II. The curve is the regression line of the experimental compression set and crosslinking data of Tables 2 and 3 (0 dose) for those rubbers prepared specifically for this second compression set study, those not identified by footnote symbol b in Table 2. The curve is defined by Eq. 5:

$$S = -0.77 \times 10^{-18} C_o + 95.2 \tag{5}$$

Each data point represents the average from triplicate compression sets and triplicate solvent-swollen specimens. The blank factor (Eq. 3) was determined with triplicates.

The relationships between compression set and initial cure defined by Eq. 4 (Procedure I) and Eq. 5 (Procedure II) have identical intercepts and vary by 14 % in slope. This is a reflection of the fact that the majority of the chemical additives in Procedure II exhibited little or no anti-rad or radiation-sensitizing characteristics. Procedure I, involving no chemical additives, is considered to be the more basic procedure; accordingly, Eq. 4 is used herein for predicting compression set values from corsslinking values.

The relationship between compression set and initial cure was also determined through Procedure II by combining data of the previous and present study, that is, by using compression set and crosslinking data for all additive rubbers listed in Table 2. The data of the previous study were made to conform to those of the present one by re-calculating compression sets for unheated specimens. Equation 6 is the regression line.

$$S = -0.88 \times 10^{-18} C_o + 97.5 \tag{6}$$

Equation 6 is not considered as reliable as Eqs. 4 and 5, since the crosslinking values of the previous study were determined with only a single specimen.

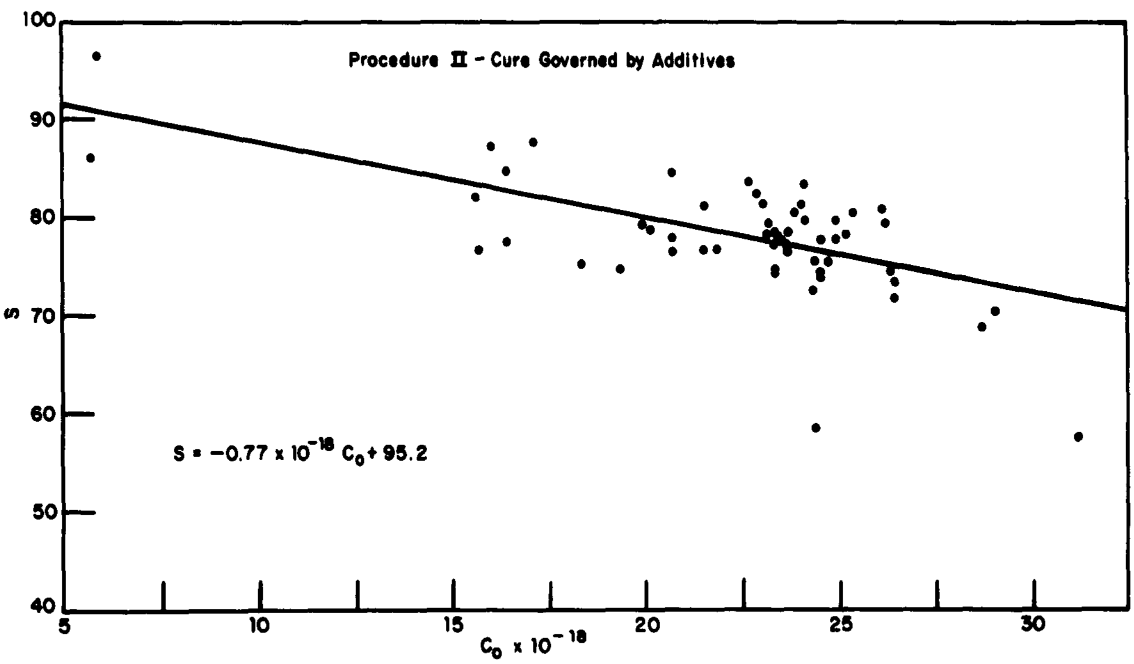


Fig. 2 Compression Set at $10^8$ r Versus Pre-Irradiation Crosslinks - Procedure II

## Anti-Rad Study

Anti-rad behavior is demonstrated when the experimental compression set is significantly less than that predicted from the initial crosslinking by Eq. 4 (Fig. 1). A comparison of experimental and calculated compression sets in Table 2 shows with 95 % confidence that phenanthrenequinone and 1,4-naphthoquinone definitely qualify as anti-rads at a $10^8$ r dose, but that the following additives barely qualify at this level of confidence and are, thus, of questionable status: 2, 2'-bipyridine; acridine; 1,2-naphthoquinone; 1,3-di-o-tolylquanidine.

It is of interest that 9,10-phenanthrenequinone and 1,4-naphthoquinone exhibit anti-rad behavior, decreasing compression set in rubber at $10^8$ r; that 1,2-naphthoquinone barely or questionably does; and that 1, 4-benzoquinone and anthraquinone do not.

2,2-Diphenyl-1-picrylhydrazyl was not an anti-rad. This material exists completely as diphenylpicrylhydrazyl radicals in the solid state. One would expect these radicals in a vulcanizate to react with free radicals produced in the rubber hydrocarbon by irradiation and, thus, block radical-engendered crosslinking and scission. Probably diphenylpicrylhydrazyl radicals were never present in the vulcanizate, having been destroyed by reacting with radicals produced in the rubber by mill-mixing and curing.

No anti-rads have ever been found which will perform at a $10^9$ r dose. Because $10^9$ r would require a 5300-hr exposure to the cobalt-60 source, the potential anti-rads were screened at $10^8$ r with the intention of testing at $10^9$ r those which showed promise. 9,10-phenanthrenequinone and 1,4-naphthoquinone qualify for testing at $10^9$ r. Only anti-rads which cause an appreciable reduction in compression set at $10^9$ r would be of practical value.

## Chain Scission and Crosslinking

The total number of crosslinks per gram for a compressed specimen before irradiation and after doses of $10^7$ and $10^8$ r are given in Table 3. These data show that, depending upon the additive, crosslinking may predominate over or be balanced by chain scission up to $10^7$ r, but that crosslinking always predominates at $10^8$ r. Crosslinking increases enormously between $10^8$ and $10^9$ r, so that specimens become brittle or glassy, or shrink to give compression sets over 100 %.

Table 3 gives radiation yields for scission of the original network and radiation yields for concurrent crosslinking to form a new network conforming to the compressed state. These yields, G(S) and G(C),

TABLE 3

Crosslinking Values and Radiation Yields

| Vulcanizate (Additive Rubbers Designated by Additive) | Foot-notes | Total Crosslinks Per Gram $C_o$ ($\times 10^{-18}$) | C ($\times 10^{-18}$) | | Decrease in Vulcanization Crosslinks per Gram, $\Delta C_o$ for $10^8$ r Dose ($\times 10^{-18}$) | Radiation-Induced Crosslinks Per Gram, $C_r$ for $10^8$ r Dose ($\times 10^{-18}$) | Radiation Yield Between 0 to $10^7$ r | |
|---|---|---|---|---|---|---|---|---|
| | | 0 Dose | $10^7$ r | $10^8$ r | | | G(Scission) | G(Crosslinking) |
| 9,10-Phenanthrenequinone | a | 31.2 | 29.3 | 34.7 | 16.6 | 20.[illegible] | 1.2 | 0.81 |
| 1,4-Naphthoquinone | a | 24.4 | 23.9 | 28.8 | 13.0 | 17.1 | 0.55 | 0.41 |
| 2,2'-Bipyridine | b,c | 28.7 | 30.7 | 38.1 | 17.7 | 26.9 | 1.0 | 1.5 |
| 2-Amino-4-Methylpyridine | b,c | 29.0 | 30.5 | 39.1 | 18.6 | 28.0 | 0.98 | 1.1 |
| Triphenylstilbine | a | 26.4 | 26.4 | 38.0 | 16.7 | 28.1 | 1.6 | 1.5 |
| 2,4-Dinitrophenylhydrazine | a | 24.3 | 27.8 | 34.8 | 15.5 | 25.6 | 0.27 | 0.51 |
| o-Aminophenol | a | 26.4 | 28.4 | 35.6 | 17.1 | 26.3 | 0.66 | 0.96 |
| Biphenyl | a | 24.5 | 28.0 | 35.3 | 15.7 | 26.4 | 0.34 | 0.94 |
| Pyrene | a | 23.3 | 27.0 | 33.0 | 14.8 | 25.2 | 0.62 | 1.2 |
| Phenyl Sulfide | a | 24.5 | 27.3 | 32.6 | 16.5 | 24.5 | 0.69 | 1.1 |
| Fluoranthrene | a | 23.3 | 26.2 | 30.9 | 15.4 | 23.2 | 0.65 | 1.1 |
| Hydroquinone | a | 26.3 | 30.4 | 36.9 | 17.0 | 27.7 | 0.39 | 1.1 |
| Acridine | b,c | 19.3 | 23.8 | 33.4 | 11.4 | 25.4 | 0.56 | 1.3 |
| 1,2-Naphthoquinone | a | 18.3 | 21.5 | 34.1 | 10.7 | 26.6 | 0.45 | 0.97 |
| Triphenyl Bismuthine | a | 24.7 | 24.6 | 36.3 | 16.5 | 27.8 | 1.3 | 1.3 |
| 2,2-Diphenyl-1-picrylhydrazyl | a | 24.4 | 26.3 | 32.3 | 17.3 | 24.7 | 0.63 | 0.85 |
| Butyl Disulfide | a | 20.7 | 22.0 | 24.6 | 15.3 | 19.1 | 0.93 | 1.1 |
| Phenanthrene | a | 23.7 | 27.0 | 32.4 | 16.2 | 25.0 | 0.72 | 1.3 |
| N-Cyclohexyl-N'-phenyl-p-phenylenediamine | b,c | 21.5 | 24.0 | 31.8 | 14.8 | 25.0 | 0.48 | 0.89 |
| 1,3-Di-o-tolylguanidine | b,c | 15.7 | 19.0 | 25.4 | 11.3 | 20.8 | 0.71 | 1.2 |
| N-Phenyl-N'-isopropyl-p-phenylenediamine | c | 21.8 | 24.1 | 33.2 | 14.6 | 25.8 | 0.47 | 0.83 |
| p-Quaterphenyl | a | 23.6 | 27.4 | 38.1 | 15.8 | 29.7 | 0.79 | 1.4 |
| m-Terphenyl | a | 23.3 | 26.5 | 34.7 | 15.8 | 27.0 | 0.76 | 1.3 |
| Phenyl Disulfide | a | 16.4 | 17.8 | 21.8 | 11.8 | 17.1 | 0.58 | 0.83 |

(Continued)

TABLE 3 (Contd)

Crosslinking Values and Radiation Yields

| Vulcanizate (Additive Rubbers Designated by Additive) | Foot-notes | Total Crosslinks Per Gram $C_o$ ($\times 10^{-18}$) | C ($\times 10^{-18}$) | | Decrease in Vulcanization Crosslinks per Gram, $\Delta C_o$ for $10^8$ r Dose ($\times 10^{-18}$) | Radiation-Induced Crosslinks Per Gram, $C_r$ for $10^8$ r Dose ($\times 10^{-18}$) | Radiation Yield Between 0 to $10^7$ r | |
|---|---|---|---|---|---|---|---|---|
| | | 0 Dose | $10^7$ r | $10^8$ r | | | G(Scission) | G(Crosslinking) |
| p-Terphenyl | a | 23.5 | 27.1 | 36.5 | 15.6 | 28.5 | 0.86 | 1.5 |
| Triphenylmethane | a | 24.5 | 27.7 | 35.3 | 16.9 | 27.7 | 0.73 | 1.3 |
| iso-Butyl Sulfide | a | 20.7 | 23.0 | 26.9 | 14.9 | 21.2 | 0.81 | 1.2 |
| p-Aminophenol | a | 24.9 | 27.8 | 38.0 | 17.2 | 29.8 | 0.76 | 1.2 |
| Chrysene | a | 23.4 | 27.5 | 35.8 | 15.8 | 28.3 | 0.80 | 1.5 |
| Diphenylmercury | a | 31.7 | 34.3 | 35.7 | 24.6 | 28.5 | 1.2 | 1.7 |
| Cystine | a | 25.2 | 27.4 | 37.7 | 17.4 | 29.6 | 0.74 | 1.2 |
| Naphthalene | a | 23.1 | 26.4 | 35.8 | 15.7 | 28.2 | 0.66 | 1.2 |
| Phenol | a | 23.3 | 26.0 | 39.1 | 15.7 | 31.2 | 1.1 | 1.5 |
| iso-Butyl Disulfide | a | 23.7 | 27.1 | 35.8 | 16.5 | 28.1 | 0.79 | 1.3 |
| Dicylohexylamine | b,c | 20.1 | 27.9 | 33.9 | 14.4 | 28.2 | 0.56 | 1.9 |
| 4,4'-Oxydiphenol | a | 26.2 | 30.4 | 38.6 | 18.9 | 30.9 | 0.83 | 1.4 |
| Dibutyltin Dichloride | a | 19.9 | 24.0 | 28.9 | 14.5 | 23.3 | 0.85 | 1.5 |
| o-Terphenyl | a | 23.2 | 26.5 | 34.2 | 16.4 | 27.3 | 0.55 | 1.2 |
| Anthraquinone | a | 24.1 | 26.6 | 34.3 | 17.7 | 27.5 | 0.83 | 1.2 |
| Resorcinol | a | 24.9 | 27.7 | 37.7 | 17.7 | 30.4 | 0.95 | 1.4 |
| Butyl Sulfide | a | 23.8 | 27.1 | 36.2 | 16.8 | 29.3 | 0.86 | 1.4 |
| P, P'-Biphenol | a | 25.3 | 29.1 | 35.4 | 19.0 | 28.7 | 0.96 | 1.5 |
| Tetrabutyl Tin | a | 26.1 | 29.0 | 36.3 | 20.4 | 29.6 | 0.81 | 1.2 |
| N,N'-Dicarbethoxyhydrazine | a | 21.5 | 24.5 | 38.0 | 14.9 | 31.1 | 1.2 | 1.6 |
| Tetraphenyl Tin | a | 24.0 | 27.6 | 36.0 | 17.7 | 29.6 | 0.92 | 1.4 |
| Anthracene | a | 23.0 | 26.4 | 36.8 | 16.5 | 30.2 | 0.91 | 1.4 |
| Tetraethyl Orthotitanate | a | 15.6 | 18.1 | 36.1 | 10.3 | 30.5 | 0.98 | 1.3 |
| Dibutyltin Diacetate | a | 22.9 | 26.8 | 26.0 | 18.6 | 21.8 | 0.55 | 1.2 |
| Hydrazine Sulfate | a | 24.1 | 25.4 | 36.6 | 18.4 | 30.9 | 1.1 | 1.3 |
| Triphenyltin Chloride | a | 22.7 | 25.6 | 36.8 | 17.4 | 31.2 | 1.2 | 1.6 |
| Tetraethyl Orthosilicate | a | 20.7 | 23.7 | 35.7 | 15.2 | 30.6 | 0.95 | 1.5 |
| 1,2,3-Triketohydrindene | a | 16.4 | 20.7 | 28.2 | 12.7 | 24.5 | 0.70 | 1.4 |

(Continued)

TABLE 3 (Contd)

Crosslinking Values and Radiation Yields

| Vulcanizate (Additive Rubbers Designated by Additive) | Foot-notes | Total Crosslinks Per Gram $C_o$ ($\times 10^{-18}$) 0 Dose | C ($\times 10^{-18}$) $10^7$ r | C ($\times 10^{-18}$) $10^8$ r | Decrease in Vulcanization Crosslinks per Gram, $\Delta C_o$ for $10^8$ r Dose ($\times 10^{-18}$) | Radiation-Induced Crosslinks Per Gram, $C_r$ for $10^8$ r Dose ($\times 10^{-18}$) | Radiation Yield Between 0 to $10^7$ r G(Scission) | Radiation Yield Between 0 to $10^7$ r G(Crosslinking) |
|---|---|---|---|---|---|---|---|---|
| 2-Aminobenzimidazole | b,c,d | 5.7 | 12.3 | 23.4 | - | - | - | - |
| m-Aminophenol | a | 16.0 | 20.8 | 32.4 | 15.6 | 32.0 | 0.79 | 1.6 |
| Phloroglucinol | a | 17.1 | 23.1 | 32.7 | 15.2 | 31.0 | 0.62 | 1.7 |
| 1,4-Benzoquinone | a | 5.8 | 12.6 | 24.7 | 5.7 | 24.6 | 0.23 | 1.4 |
| Stock 1 (6.5 min. cure-no additive) | c,d | 7.8 | 22.0 | 27.7 | - | - | - | - |
| Stock 2 (7 min. cure-no additive) | c,d | 8.1 | 20.6 | 27.4 | - | - | - | - |
| Stock 3 (7.5 min. cure-no additive) | c,d | 8.5 | 23.8 | 26.2 | - | - | - | - |
| Stock 4 (8 min. cure-no additive) | c,d | 9.5 | 23.1 | 28.9 | - | - | - | - |
| Stock 5 (8.5 min. cure-no additive) | c,d | 10.3 | 23.3 | 27.6 | - | - | - | - |
| Stock 6 (9 min. cure-no additive) | c,d | 10.7 | 24.4 | 28.5 | - | - | - | - |
| Stock 7 (9.5 min. cure-no additive) | c,d | 14.8 | 25.1 | 28.4 | - | - | - | - |
| Stock 8 (10 min. cure-no additive) | c,d | 20.3 | 28.1 | 31.0 | - | - | - | - |
| Stock 9 (15 min. cure-no additive) | c | 23.0 | 29.3 | 32.9 | 17.2 | 27.2 | 0.18 | 1.3 |
| Stock 10 (20 min. cure-no additive) | c | 23.5 | 28.6 | 33.8 | 17.7 | 27.8 | 0.60 | 1.4 |
| Stock 12 (25 min. cure-no additive) | c | 23.2 | 29.0 | 35.8 | 16.4 | 29.2 | 0.53 | 1.5 |
| Stock 13 (30 min. cure-no additive) | c | 22.7 | 28.2 | 35.0 | 14.4 | 27.6 | 0.34 | 1.3 |
| Stock 14 (35 min. cure-no additive) | c | 22.6 | 28.4 | 35.8 | 15.0 | 28.0 | 0.38 | 1.4 |

a. Each value of $C_o \times 10^{-18}$ and $C \times 10^{-18}$ is the average of a triplicate solvent swelling experiment. Values of $\Delta C_o \times 10^{-18}$, $C_r \times 10^{-18}$ and radiation yields were calculated by combining data from triplicate solvent swelling and triplicate compression set experiments.

b. The results for this additive rubber were not taken or re-calculated from the previous report.[1] New test specimens were prepared for this study.

c. Each value of $C_o \times 10^{-18}$ and $C \times 10^{-18}$ is the average of a quintuplicate solvent swelling experiment. Values of $\Delta C_o \times 10^{-18}$, $C_r \times 10^{-18}$ and radiation yields were calculated by combining data from quintuplicate solvent swelling and quintuplicate compression set experiments.

d. G values could not be calculated. Significant specimen flow under compression made the equations for calculating $\Delta C_o$, $C_r$ and G values inapplicable. Values of G(Scission) turned out negative.

respectively, are defined as the number of chains scissioned or net crosslinks formed per 100 ev of absorbed energy. G(S) and G(C) do not vary significantly with additive. They accord well with the yields of the previous report,[1] and the average values of Table 3 are 0.75 and 1.3, respectively. Radiation yields were determined by the method combining compression-set and solvent-swelling measurements[1] for $10^7$ r. They are not determined with a dose as great as $10^8$ r because their nonlinearity with dose leads to an unrealistic average value. They are not determined with a dose less than $10^7$ r because specimen set would be too small for reliable measurement. Furthermore, they are not determined reliably when there is appreciable specimen flow under compression, since the equation (Eq. 11, ref. 1) that incorporates the set length $\ell_s$ and is required for calculating radiation yields is theoretically inapplicable when specimens flow. Specimen flow is revealed by blank factors which depart significantly from unity. This inapplicability is actually seen when values of G(S) turn out to be negative in cases where specimens flow. The blank factors of Table 1 show that specimen flow is significant below a pre-irradiation cross-linking density of $20 \times 10^{18}$ crosslinks per gram.

Both the number of pre-irradiation (vulcanization) crosslinks scissioned by radiation and the number of crosslinks formed by radiation in the compressed state depend upon the degree of initial cure. The relationships are defined by Eqs. 7 and 8, and are depicted in Fig. 3:

$$\Delta C_o = 0.60\ C_o + 2.4 \times 10^{18} \qquad (7)$$

$$C_r = 0.26\ C_o + 21.5 \times 10^{18} \qquad (8)$$

where $C_o$ = Number of initial (vulcanization) crosslinks per gram of specimens.

$\Delta C_o$ = Number of vulcanization crosslinks scissioned per gram of specimen by $10^8$ r.

$C_r$ = Number of crosslinks engendered per gram of specimen in the compressed state by $10^8$ r.

These curves are the regression lines of the data for $\Delta C_o$, $C_r$, and $C_o$ in Table 3, except that the data for 9, 10-phenanthrenequinone, 1,4-naphthoquinone, and 1,4-benzoquinone were omitted since the former two were anti-rads and the latter had a low cure conducive to specimen flow. These relationships result from the fact that as initial crosslinking density increases, the probability of scission increases and the probability for crosslinking increases due to greater proximity of hydrocarbon chains.

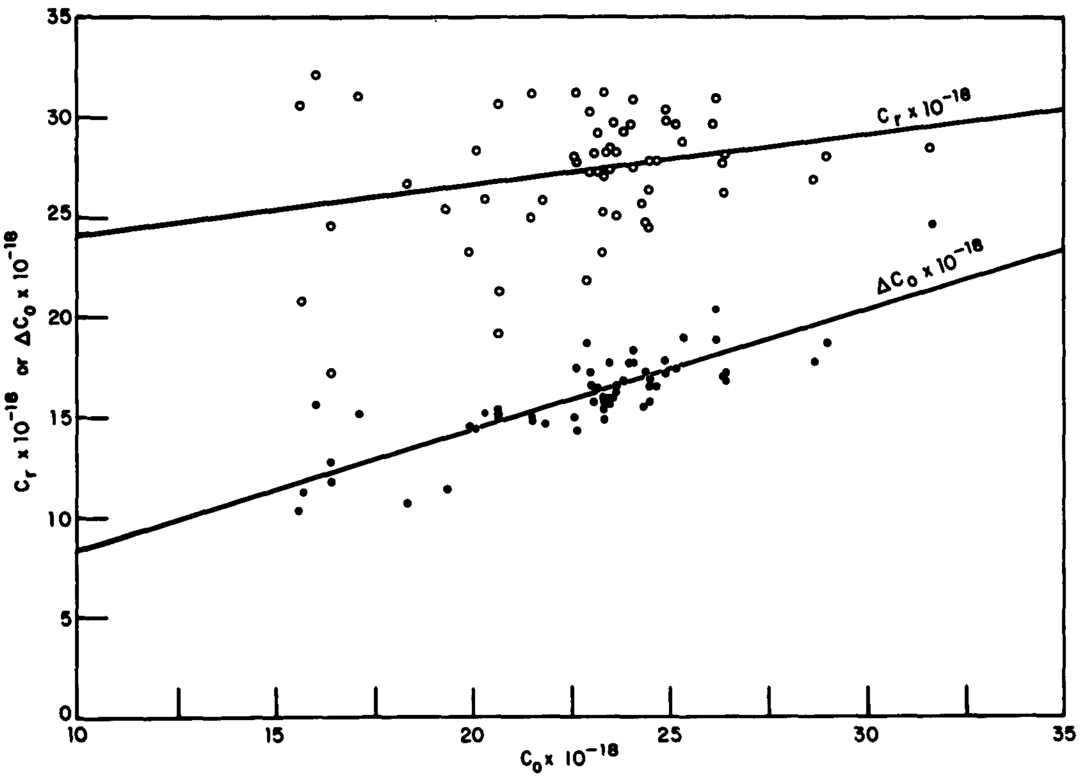


**Fig. 3** Crosslinks Formed in Compressed State ($C_r$) by $10^8$ r Versus Pre-Irradiation Crosslinks
and
Vulcanization Crosslinks Scissioned ($\Delta C_o$) by $10^8$ r Versus Pre-Irradiation Crosslinks

Anti-rads may be identified by incorporating them into pellets and measuring the sum of $\Delta C_o$ and $C_r$. There is evidence of anti-rad behavior when the experimental sum is significantly less than that predicted from Eqs. 7 and 8 on the basis of degree of cure. The basis for this is that cleavage of the initial (vulcanization) network and crosslinking to form a new network of the compressed state both promote set. An anti-rad must function by minimizing these processes which are measured by $\Delta C_o$ and $C_r$. 9,10-Phenanthrenequinone and 1,4-naphthoquinone were identified as anti-rads by means of compression set. Their values of $(\Delta C_o + C_r)$ are $36.9 \times 10^{18}$ and $30.1 \times 10^{18}$, respectively (Table 3), which are below the values predicted from degree of cure ($50.6 \times 10^{18}$ and $44.7 \times 10^{18}$, respectively) and which differ from the predicted values at the 95 % confidence level.

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$$C_r = 0.26\ C_o + 21.5 \times 10^{18}$$

$$\Delta C_o = 0.60\ C_o + 2.4 \times 10^{18}$$

where S = Percent compression set

$C_o$ = Number of vulcanization crosslinks per gram of specimen (degree of vulcanization)

$C_r$ = Number of crosslinks engendered per gram of specimen in the compressed state by $10^8$ r

$\Delta C_o$ = Number of vulcanization crosslinks scissioned per gram by $10^8$ r.

The average radiation yield (G) for chain scission and for crosslinking in the dose region from 0 to $10^7$ r was 0.75 and 1.3, respectively. 9, 10-Phenanthrenequinone and 1, 4-naphthoquinone functioned as anti-rads at $10^8$ r and reduced compression set moderately below that predicted from degree of cure. UNCLASSIFIED


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where S = Percent compression set

$C_o$ = Number of vulcanization crosslinks per gram of specimen (degree of vulcanization)

$C_r$ = Number of crosslinks engendered per gram of specimen in the compressed state by $10^8$ r

$\Delta C_o$ = Number of vulcanization crosslinks scissioned per gram by $10^8$ r.

The average radiation yield (G) for chain scission and for crosslinking in the dose region from 0 to $10^7$ r was 0.75 and 1.3, respectively. 9, 10-Phenanthrenequinone and 1, 4-naphthoquinone functioned as anti-rads at $10^8$ r and reduced compression set moderately below that predicted from degree of cure. UNCLASSIFIED

$$S = -0.66 \times 10^{-18} C_o + 95.1$$

$$C_r = 0.26\ C_o + 21.5 \times 10^{18}$$

$$\Delta C_o = 0.60\ C_o + 2.4 \times 10^{18}$$

where S = Percent compression set

$C_o$ = Number of vulcanization crosslinks per gram of specimen (degree of vulcanization)

$C_r$ = Number of crosslinks engendered per gram of specimen in the compressed state by $10^8$ r

$\Delta C_o$ = Number of vulcanization crosslinks scissioned per gram by $10^8$ r.

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